



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/SE88/00469 <b>(22) International Filing Date:</b> 12 September 1988 (12.09.88)  <b>(31) Priority Application Number:</b> 8703561-4 <b>(32) Priority Date:</b> 15 September 1987 (15.09.87) <b>(33) Priority Country:</b> SE  <b>(71) Applicant:</b> KEMANORD INDUSTRIKEMI AB [SE/SE]; Box 13000, S-850 13 Sundsvall (SE).  <b>(72) Inventors:</b> MELLSTRÖM, Rolf ; Gärdesvägen 192, S-840 10 Ljungaverk (SE). ANDERSSON, Olaus ; Egnahemsvägen 6, S-840 10 Ljungaverk (SE). ÅHLUND, Göran ; Ångsvägen 13, S-840 10 Ljungaverk (SE). JOHANSSON, Ingemar ; Tälje 4205, S-840 21 Erikslund (SE).		<b>(74) Agent:</b> SCHÖLD, Zaid; Nobel Industries Sweden AB, Patents Department, Box 11554, S-100 61 Stockholm (SE).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), NO, SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR THE PURIFICATION OF SILICON  <b>(57) Abstract</b>  The invention concerns a method for purifying silicon from boron by treating crude silicon with molten slag. Silicon is contacted with a slag, the slag-forming components of which consist of solid chlorine compounds and at least one compound selected from the group consisting of oxides, hydroxides, carbonates of alkali and/or alkaline earth metals as well as silica. Chlorides of alkali and/or alkaline earth metals can be used as solid chlorine compound.		

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METHOD FOR THE PURIFICATION OF SILICON

The present invention relates to a method for the purification of silicon. More particularly, the invention comprises a method for purifying metallurgical silicon for the production of raw materials for the semiconductor and solar cell industry.

To make the electric energy produced by solar cells economically competitive, the silicon from which the solar cells are made must be relatively inexpensive. In the production of silicon for electronics components, purification by gaseous phase is used. This technique is far too expensive for the production of solar cells. However, since the purity requirements placed on solar cell silicon are not as high as for silicon for electronic uses, simpler purification techniques can be used.

U.S. patent specification 4,304,763 discloses a multiple step method for purifying metallurgical silicon. Finely divided silicon is leached with acid, whereupon it is melted and subjected to vacuum evaporation at 1500°-1700°C. If there is a high content of contaminating boron, molten silicon is contacted with a molten slag which may consist of a mixture of  $\text{CaF}_2$ ,  $\text{CaO}$  and  $\text{SiO}_2$ .

Solar cell silicon is defined by its property of converting light energy with an efficiency of at least 10%. Foreign elements affect the efficiency differently. Producers of solar cell silicon have especially wished for a boron reduction to 1-5 ppmw in the starting material, and this has not been possible with the prior art techniques referred to above.

The present invention as defined by the claims indicates an improved method for the purification of silicon from boron by treating crude silicon with a molten slag. This method gives a higher degree of

purification and utilises a less poisonous melt than the above-mentioned method. A further advantage is that the amount of slag-forming agents employed is considerably lower than in prior art methods. For example, the above-mentioned U.S. patent uses an amount of slag which is twice as large as the amount of silicon that is being processed.

Solid chlorine compounds are used as the active slag-forming component. As solid chlorine compounds, chlorides of alkali and/or alkaline earth metals may be used, such as sodium, potassium or lithium chloride, or calcium, magnesium, barium or strontium chloride. Other conceivable solid chlorine compounds are hypochlorites, chlorates or perchlorates of alkali and/or alkaline earth metals.

Other constituents of the slag which may be present are oxides of alkali and/or alkaline earth metals, and silica. Further constituents that can be used are oxide-forming carbonates and hydroxides of alkali and alkaline earth metals.

The slag-forming agent has essentially three functions. It constitutes the extraction phase, i.e. some impurities pass from the silicon phase into the slag phase. It eliminates losses in the form of heat as well as losses in the form of silicon, the latter being caused by splashes from the silicon surface and oxidation thereof.

The active component binds boron in the form of volatile boron chlorides. The slag is oxidising in the electrochemical sense, which increases the valency of boron from 0 to +III, thus facilitating the formation of B(III)chlorides.

The method is preferably carried out such that silicon is melted and heated to 1500-1600°C in a melting furnace, whereupon the slag-forming agent is added. The particle size of the slag-forming agent is not critical, but less fumes and less dust are

obtained if coarser materials are used. A suitable particle size lies within the range 1-3 mm. The slag-forming agent may be added in one or several runs. After the slag has been added, the melt is again heated to 1500-1600°C. Normally, no longer contact time is required. After the desired number of slag treatments has been carried out, the silicon is teemed, crushed and allowed to cool and then analysed. Thus, the silicon need not first be finely ground and mixed with the slag-forming agent and then heated, as indicated by other prior art methods. The method is therefore suitable for purifying liquid metallurgical silicon directly after a reduction furnace.

The slag treatment may take place in a conventional melting furnace, for example in an arc furnace or an induction furnace. The furnace is important to the process in so far as it increases the temperature of the material to be processed to a suitable processing temperature.

The temperature is an important parameter of the purification process. High temperature means high purification, whereas low temperature gives no purification. A suitable processing temperature is from 1410°C, preferred temperatures lying between 1500°C and 1600°C. The higher the temperature, the higher will be the purification efficiency, the upper limit being set by production engineering factors.

The quantity ratio between slag and crude silicon based on weight may be 0.1-2, preferably 0.5-1. The composition of the slag suitably is 0.1-50% by weight of solid chlorine compounds, 0-50% by weight of at least one compound selected from the group consisting of oxides, carbonates and hydroxides of alkali and/or alkaline earth metals, and 0-80% by weight of silica. Preferred values are 10-30% by weight of solid chlorine compounds, 10-30% by weight of at least one compound selected from the group consisting of oxides, carbonates and

hydroxides of alkali and/or alkaline earth metals, and 40-70% by weight of silica. The values most preferred are 20, 20 and 60% by weight, respectively.

After addition of the slag-forming agent and heating for the desired period of time, the melt in the furnace consists of two phases, a lower silicon phase and an upper slag phase. Thus, the slag is a top slag. To be able to separate the silicon from the slag, it may be necessary to allow the slag to cool somewhat to cause it to set.

The silicon obtained by the method according to the invention has a far higher degree of purification than silicon purified by prior art techniques employing slag purification. The boron content, in particular, can be lowered from about 16 ppmw to about 5 ppmw.

It has also been found that a considerable purification of the carbon content is achieved. The purification of carbon is especially advantageous if performed in an arc furnace. In an induction furnace, silicon is contaminated by carbon from the graphite lining. However, in order to achieve an especially high degree of purification for the remaining impurities, it is necessary to couple the method according to the invention with a known acid and/or vacuum treatment.

The invention will now be described in more detail in the following Examples.

#### Example 1

Equipment: Arc furnace with injection equipment in the form of a graphite lance.

A hot ladle was filled with about 1700 kg commercial silicon. The ladle was heated in the arc furnace for about 50 min, after which the temperature was about 1600°C. Then about 1/3 of  $\text{CaCl}_2$ , and after that 1/3 of a mixture of  $\text{CaO}$  and  $\text{SiO}_2$  were charged. The procedure was repeated 2 times until all slag-forming agent, in all 1400 kg, had been added. The slag-forming

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agent consisted of 275 kg  $\text{CaCl}_2$ , 250 kg  $\text{CaO}$ , and 875 kg  $\text{SiO}_2$ . After the melt had been further heated for about 30 min, the ladle was allowed to cool until the slag had set to such an extent that silicon could be teemed without slag admixture. The silicon charged was analysed both before and after purification. The result is shown in Table 1.

Table 1:

	<u>Impurity content</u>					
	B	Fe	Al	Ca	Cl	C
	ppmw	%	%	%	%	%
15 <u>Silicon charged</u>	13	0.26	0.60	0.12	0.01	0.08
<u>Silicon teemed</u>	6	0.37	0.07	0.05	0.01	0.01

It appears from the Table that the boron content is reduced from 13 ppmw in commercial silicon to 6 ppmw in purified silicon.

Example 2

Equipment: Induction furnace with graphite crucible.

25        300 g silicon are melted and heated to 1500-1600°C. One third of the slag-forming agent which consisted of 50 g  $\text{CaCl}_2$ , 50 g  $\text{CaO}$  and 175 g  $\text{SiO}_2$ , was added, After that, heating to 1500-1600°C was again carried out, and the melt was held for about 30 min. Two further slag admixtures were carried out in the same manner. The finished silicon was teemed, allowed to cool and analysed. The result is shown in Table II.

Table 2:

		<u>Impurity content</u>					
5		B	Fe	Al	Ca	Cl	C
		ppmw	%	%	%	%	%
	<u>Silicon charged</u>	17	0.31	0.29	0.04	-	0.06
10	<u>Silicon teemed</u>	5	0.42	0.66	0.08	0.09	0.14

It appears from the Table that the boron content is reduced from 17 to 5 ppmw ("ppmw" means parts per million based on weight).



## CLAIMS

1. A method for purifying silicon from boron, by treating crude silicon with molten slag, c h a r a c -  
t e r i s e d in that silicon is contacted with a slag  
in which one of the slag-forming components consists  
5 of a solid chlorine compound.

2. A method as claimed in claim 1, c h a r a c -  
t e r i s e d in that molten silicon is contacted  
with the slag.

3. A method as claimed in claim 1, c h a r a c -  
10 t e r i s e d in that solid chlorine compounds and  
at least one compound selected from the group consisting  
of oxides, carbonates and hydroxides of alkali and/or  
alkaline earth metals as well as silica are used as  
slag-forming components.

4. A method as claimed in claim 3, c h a r a c -  
15 t e r i s e d in that the slag contains 0.1-50% by  
weight of solid chlorine compounds, 0-50% by weight  
of at least one compound selected from the group con-  
sisting of oxides, carbonates and hydroxides of alkali  
20 and/or alkaline earth metals, as well as 0-80% by  
weight of silica.

5. A method as claimed in claim 1, c h a r a c -  
t e r i s e d in that the ratio between the amount  
of slag and the amount of crude silicon, based on  
25 weight, is 0.1-2.

6. A method as claimed in claim 3, c h a r a c -  
t e r i s e d in that chlorides of alkali and/or alka-  
line earth metals are used as solid chlorine compounds.

7. A method as claimed in claim 6, c h a r a c -  
30 t e r i s e d in that  $\text{CaCl}_2$  in an amount of 10-30%  
by weight of the slag is used as chloride.

8. A method as claimed in claim 3, c h a r a c -  
t e r i s e d in that  $\text{CaO}$  is used as oxide-containing  
compound.

9. A method as claimed in claim 2, c h a r a c -  
t e r i s e d in that the treatment temperature is  
from 1410°C, preferably above 1500°C.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/SE88/00469

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <sup>4</sup> <div style="text-align: center; font-family: monospace; font-size: 1.2em;">C 01 B 33/02</div>								
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; font-size: 0.8em;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black; font-size: 0.8em;">Classification System</th> <th style="border-bottom: 1px solid black; font-size: 0.8em;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px; vertical-align: top;">           IPC 4            US C1         </td> <td style="padding: 5px; vertical-align: top;">           C 01 B 33/00, /02  <u>423</u>: 348, 350         </td> </tr> </table> <div style="text-align: center; font-size: 0.8em; margin-top: 5px;">           Documentation Searched other than Minimum Documentation            to the Extent that such Documents are Included in the Fields Searched <sup>8</sup> </div> <div style="padding: 10px; font-family: monospace; font-size: 1.1em;">           SE, NO, DK, FI classes as above         </div>			Classification System	Classification Symbols	IPC 4 US C1	C 01 B 33/00, /02 <u>423</u> : 348, 350		
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse; font-size: 0.8em;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category <sup>10</sup></th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with Indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="vertical-align: top; padding: 10px;">A</td> <td style="vertical-align: top; padding: 10px;">           DE, A1, 2 933 164 (CONSORTIUM FÜR ELEKTROCHEMISCHE            INDUSTRIE GMBH)            26 February 1981         </td> <td style="vertical-align: top; padding: 10px;">1-9</td> </tr> </table> <div style="font-size: 0.8em; margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div> </div>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with Indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	DE, A1, 2 933 164 (CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GMBH) 26 February 1981	1-9
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<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;">           Date of the Actual Completion of the International Search  <div style="text-align: center; font-family: monospace; font-size: 1.1em;">1988-11-09</div> </td> <td style="width: 50%; padding: 5px; vertical-align: top;">           Date of Mailing of this International Search Report  <div style="text-align: center; font-family: monospace; font-size: 1.1em;">1988 -11- 23</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;">           International Searching Authority  <div style="text-align: center; font-family: monospace; font-size: 1.1em;">Swedish Patent Office</div> </td> <td style="width: 50%; padding: 5px; vertical-align: top;">           Signature of Authorized Official  <div style="text-align: center;"> <div style="text-align: center; font-family: monospace; font-size: 1.1em;">May Hallne</div> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-family: monospace; font-size: 1.1em;">1988-11-09</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-family: monospace; font-size: 1.1em;">1988 -11- 23</div>	International Searching Authority <div style="text-align: center; font-family: monospace; font-size: 1.1em;">Swedish Patent Office</div>	Signature of Authorized Official <div style="text-align: center;"> <div style="text-align: center; font-family: monospace; font-size: 1.1em;">May Hallne</div> </div>		
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